CHAPTER III
EFFECT OF OXYGEN DEFICIENCY IN THE Y123 SYSTEM
III.1 Introduction

As described in chapter 1, the family of compounds $YBa_2Cu_3O_{7-\delta}$, generally known as 123 compounds, exhibit superconductivity in the 90K range. The structure of these compounds consists of an orthorhombically distorted perovskite with a tripled unit cell of the simple perovskite along the c axis or a closely related tetragonal form, depending on the oxygen stoichiometry.

The structures and properties of $YBa_2Cu_3O_{7-\delta}$ that are observed at and below room temperature depend critically on how the material is processed at higher temperatures. This is due to the fact that the superconducting properties are largely controlled by the oxygen content and arrangement in $YBa_2Cu_3O_{7-\delta}$ which, in turn, are controlled by the annealing times and temperatures.

Studies on $YBa_2Cu_3O_{7-\delta}$ have revealed that oxygen stoichiometry plays a vital role in the structure and properties of these materials. Studies on the prototype phase $YBa_2Cu_3O_{7-\delta}$ have revealed a stability range of $6.0 \leq 7 - \delta \leq 7.0$. Reversible changes in crystallographic symmetry and physical properties have been found to occur over this range of composition. Detailed studies of the structures, oxygen mobility and properties of $YBa_2Cu_3O_{7-\delta}$ for $6.0 \leq 7 - \delta \leq 7.0$ have provided insight into the chemical nature of these materials and into possible mechanisms for superconductivity and for crystal twinning.

Investigations of phase transformations carried out by Roth et al show clearly that the orthorhombic superconducting oxide $YBa_2Cu_3O_{7-\delta}$ transforms into a tetragonal form above 750°C, and loses oxygen above 930°C. It is also well established that superconductivity decreases as the oxygen content decreases. It has also been shown that it is possible to stabilize the tetragonal form by quenching at room temperature. It appears from x-ray diffraction [1] and neutron diffraction studies [2] that two limits exist: the orthorhombic superconductor $YBa_2Cu_3O_7$ and the tetragonal oxide $YBa_2Cu_3O_6$. However, from the chemical analysis and structural studies, it has been seen that the upper limit is rarely reached and that for different samples the oxygen content may vary between these two limits.

The orthorhombic-to-tetragonal phase transition in the 123 compound was initially identified by electron beam heating in a transmission electron microscope (TEM) [3] and subsequently studied by numerous techniques.[4-
There has been considerable speculation about the significance in superconductivity of the linear \((-\text{Cu} - \text{O})_n\) chains in the YBa$_2$Cu$_3$O$_{7-\delta}$ compounds. The composition and formal oxidation states for copper are essentially the same, yet the orthorhombic form with chains is superconducting with a $T_c$ of about 90K whereas the tetragonal form without chains is not superconducting above 4.2K. We see that superconductivity disappears in the YBa$_2$Cu$_3$O$_{7-\delta}$ system as $7 - \delta$ decreases towards 6 and the chains disappear.

It has been shown [4] that the loss of oxygen (as $\delta$ increases) takes place mainly from the O(1) site in the structure, thereby disrupting the Cu(1) – O(1) linear chains along the b direction. At the same time, some oxygens occupy the O(5) sites. For $\delta \approx 0.6$, O(1) and O(5) sites are equally occupied and become symmetry equivalent. This results in a structural transition to the tetragonal phase with equal a and b values. Further increase in $\delta$ reduces the occupancy of both sites equally until, at $\delta = 1$, both sites are empty. To obtain the optimum oxygen values, the annealing temperatures, annealing atmosphere and cooling rates are very critical during the preparation of these compounds.

Qualitatively it is known that the superconducting properties of copper oxides are sensitive to the oxygen stoichiometry, [16-22] but quantitative relationships are not known. In this work we have studied the effect of oxygen stoichiometry on the crystallographic and superconducting properties of the YBa$_2$Cu$_3$O$_{7-\delta}$ system.

### III.2 Experimental

Pure YBa$_2$Cu$_3$O$_{7-\delta}$ pellets were prepared by the standard ceramic technique. Stoichiometric amounts of Y$_2$O$_3$, BaCO$_3$ and CuO in the proper cation ratios were thoroughly mixed and heated in air at 910°C for 24 hours. The resulting mixture was reground, pelletized and reheated in air at the same temperature for another 20 hours. Subsequent calcinations were done in air at 920°C and 930°C for 20 hours each with intermediate grinding and pelletizing steps. Finally the pellets were sintered in oxygen at 940°C for 24 hours and then cooled to room temperature.
During the heating of the individual oxides, the following reactions take place

\[
\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2
\]

\[
\frac{1}{2}\text{Y}_2\text{O}_3 + 2\text{BaO} + 3\text{CuO} \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6.5}
\]

In the solid state reaction, BaCO₃ decomposes completely around 920°C, but only after prolonged heating. Hence extended and repeated heating is essential to ensure that neither free nor partly decomposed BaCO₃ is left behind. Sintering of the pellets at about 940°C is an essential step to ensure better intergranular contact and good crystalline nature. Heating in flowing oxygen ensures oxygen stoichiometry close to O₆.₃₅.

In order to vary the oxygen content of the samples, the pellets were annealed in a nitrogen atmosphere at various temperatures for 20 hours. Pellet A was annealed in nitrogen at 420°C, pellet B at 400°C and pellet C was annealed at 350°C. X-ray diffraction measurements were made at room temperature to confirm the single phase nature of these compounds and to determine their structure. Four-probe d.c. resistivity measurements were performed on bar shaped samples in the temperature range of 50K to 300K using the computer controlled resistivity setup.

### III.3 Structure of YBa₂Cu₃O₇₋₅(1−2−3) system

Soon after the discovery and confirmation of superconductivity in the Y-Ba-Cu-O [23-26] system, the phase responsible for the 90K transition was found to have a cation symmetry of 1Y:2Ba:3Cu. The unit cell dimensions determined by electron and X-ray diffraction identified the structure as being related to a cubic perovskite with one of the cube axes tripled [27-39]. In the basic perovskite structure ABO₃, there are two cation sites [40]. The A site lies at the centre of a cage formed by corner sharing anion octahedra and accommodates the larger cations in the structure. The B site lies at the centres of the anion octahedra and accommodates the smaller cations. It was therefore natural to place the larger Y and Ba ions at the A sites and the smaller Cu ions at the B sites. The tripling of the perovskite unit cell could then be accounted for by ordering the Y and Ba ions in the A sites such that the top and bottom cells, in a stack of three, contained Ba ions, while the middle cell contained a Y ion. This basic cation
arrangement was not only consistent with the 1Y:2Ba:3Cu stoichiometry but also provided a reasonable fit to X-ray diffraction data obtained from nearly single-phase materials [27-30] and accounted for contrast seen in high-resolution images of the structure [41-44]. These results confirmed that the alternative suggestion [35-39] that the structure was related to the La$_3$Ba$_3$Cu$_6$O$_{14}$ structure, proposed by Er-Rakho [45], was incorrect.

There are three anions per unit cell in the ideal perovskite structure, corresponding to nine possible oxygen sites in a tripled perovskite unit cell. Formal balancing of the charges on the cations requires a maximum of eight oxygen ions per unit cell if all of the copper is assumed to be in a +3 state, and 6.5 and 5 oxygen ions per unit cell if charges of +2 and +1 are assumed for all the copper cations. It was therefore clear that the 123 structure was oxygen deficient relative to the ideal perovskite structure. X-ray diffraction from small single crystals extracted from sintered polycrystalline material confirmed and refined the basic positions of the cations and also identified where the oxygen deficiency was accommodated in the structure [46-47]. The X-ray data showed that the Y ion was surrounded by eight oxygen ions rather than by twelve as in the case of the ideal perovskite structure. Oxygen deficiency was also noted in the basal copper plane between the Ba ions. Anion sites in this plane, which lie along the cell edges, were found to be only half occupied [30,46-47]. Refinements of the cell parameters in several studies [27-28,30,36-37,46] indicated that the unit cell was orthorhombic with b slightly larger than a, even though some single crystal studies observed a tetragonal distribution of diffracted intensities. It was noted later that this apparent discrepancy was probably caused by microdomain twinning which prevented oxygen ordering in the single crystals from being observed by X-ray diffraction techniques. The twinning was readily apparent in the transmission electron microscope (TEM) images of the material [37].

The source of the orthorhombic distortion in the 123 structure was finally revealed by neutron diffraction data using the Rietveld technique [48-56]. The neutron diffraction experiments showed unambiguously that the oxygens in the basal copper plane of the unit cell were ordered in the orthorhombic structure and that the 90K 123 material contained nearly seven oxygens per unit cell.

The effect of oxygen ordering in the basal plane of the structure is to
Fig. III.1. The structure of Y, Ba, Cu, O. In (a) the coordination of copper with oxygen is emphasized to show the location of copper-oxygen planes and chains in the structure. In (b) nearest-neighbor bonds are drawn in to show the puckering of the copper-oxygen planes. The notation used for the oxygen position in this figure is used consistently throughout the remainder of this text. Note however that the oxygen site designations are often interchanged in the literature especially the $O(1)$ and $O(4)$ sites.
occupy one of the oxygen sites along a cell edge and to leave the other site vacant. The cell edge with the occupied site is thus lengthened relative to the cell edge with the vacant oxygen site, producing an orthorhombic unit cell. The ordering puts the copper ions in the basal plane of the structure, at the centre of square arrangements of oxygen ions. The square planar arrangements of copper and oxygen ions are then linked together by sharing their corners to form "linear chains" along the b axis of the structure. Some neutron diffraction studies suggest that the chains may not be perfectly linear [57]. The effect of vacant oxygen sites around the Y ion can be seen in Fig.III.1. The absence of oxygen from the Y plane places the copper ions in the five-fold coordinated square pyramidal sites. Linking of the square bases of the pyramids at their corners results in two-dimensional puckered sheets of copper-oxygen bonds that extend in the a-b plane of the structure. The chains and planes in the structure are linked through the oxygens that lie at the apices of the square pyramids. The Y ion, which lies at the centre of the cell, is coordinated by eight oxygens that form a slightly distorted square prism. The Ba ion is 10-fold coordinated and is shifted slightly towards the Y ion relative to its position in the ideal perovskite structure.

III.3.1 Structure of YBa$_2$Cu$_3$O$_{7-\delta}$ phases

The crystallographic unit cells of the end members YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_6$ are presented in Fig.III.2. Neutron powder diffraction profile analysis indicates that the unit cell of YBa$_2$Cu$_3$O$_7$ is orthorhombic (Pmmm) with $a = 3.8198\AA$, $b = 3.8849\AA$ and $c = 11.6762\AA$[55] while that of YBa$_2$Cu$_3$O$_6$ is tetragonal (P4/mmm) with $a = 3.8570\AA$ and $c = 11.8194\AA$ [57-58]. These structures are oxygen deficient perovskites with trippled unit cells due to Ba-Y ordering along the c axis. The ordered oxygen vacancies in these structures result in a reduction in the coordination numbers of copper from the ideal six-fold octahedral coordination of a stoichiometric perovskite. For YBa$_2$Cu$_3$O$_7$, the two oxygen vacancies result in four-fold coordinate (Cu(1)) and five-fold coordinate (Cu(2)) copper atoms. This compound may be thought of as being made up of layers and chains. The Cu(1) atoms form linear chains of corner shared square planes oriented...
Fig. III.2. Schematic drawings of the unit cells of \( \text{Ba}_2\text{YC}_3\text{O}_7 \) and \( \text{Ba}_2\text{YC}_3\text{O}_6 \).

Fig. III.3. A perspective view of \( \text{Ba}_2\text{YC}_3\text{O}_7 \) emphasizing the chains of \( \text{Cu}(1) \) and layers of \( \text{Cu}(2) \).

Fig. III.4. The coordination environments and bond lengths (Å) for \( \text{Cu}(1) \) and \( \text{Cu}(2) \) in \( \text{Ba}_2\text{YC}_3\text{O}_7 \) and \( \text{Ba}_2\text{YC}_3\text{O}_6 \).
along the b axis and the Cu(2) atoms form two-dimensional layers of corner shared square pyramids as shown in Fig. III.3. The O(1) atom from the chain also serves as the apical oxygen atom for the square pyramidal Cu(2).

The structure of YBa$_2$Cu$_3$O$_6$ differs from that of YBa$_2$Cu$_3$O$_7$ by the removal of O(4) from along the b axis. This results in a change in the coordination about Cu(1) from square planar to a linear two-fold coordination. The five-fold coordination about Cu(2) is maintained. The Cu(1) – O(1) distance decreases and the Cu(2) – O(1) distance increases making Cu(2) more square planar as seen in Fig. III.4. The structure of YBa$_2$Cu$_3$O$_6$ can be described as being made of the same type of layers as in the YBa$_2$Cu$_3$O$_7$ phase but with isolated, two-coordinate, Cu(1) atoms replacing the chains.

The structures of the YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_6$ phases lend themselves to a valence description of the copper on the different crystallographic sites. The key to this description is that the linear two-fold coordination observed for Cu(1) at $7 - \delta = 6$ is typical of Cu$^{+1}$ compounds, whereas Cu$^{+2}$ and Cu$^{+3}$ may be four-, five-, or six-coordinate. The average oxidation state of copper in the end members is 2.33 for $\delta = 0$ and 1.67 for $\delta = 1$. Since Cu(2) is relatively unchanged between end members and there are two Cu(2) per formula unit, we assign it as Cu$^{+2}$ in both end members. This reasoning leads to the limiting formulas YBa$_2$Cu$^{+3}$Cu$_2$$^{+2}$O$_7$ and YBa$_2$Cu$^{+1}$Cu$_2$$^{+3}$O$_6$ for the end members and YBaCu$^{+3}$$^{(1-x)}$Cu$_x^{+1}$Cu$_2$$^{+2}$O$_{7-\delta}$ for intermediate oxygen stoichiometries. Thus Cu$^{+3}$ atoms are associated with the chains oriented along the b axis and Cu$^{+2}$ atoms associated with the layers. This further indicates that the reduction that occurs in going from O$_7$ to O$_6$ is primarily a reduction of Cu$^{+3}$ to Cu$^{+1}$ at the Cu(1) sites.

III.4 Oxygen content: The Orthorhombic - Tetragonal Transition

Both, the tetragonal and orthorhombic, structures of the YBaCuO system are derived from a regular ABX$_3$ perovskite; they differ, however, in the specific oxygen vacancy arrangements and these depend critically on preparation conditions. If this composition were referred to as a perovskite structure, its idealized composition would be YBa$_2$Cu$_3$O$_9$, which would require
an extra sheet of oxygen atoms at the Y level. Slow cooling and extensive oxygen annealing appears to produce superconducting, orthorhombic materials with high transition temperatures. We find that vacuum annealing leads to a loss in superconducting properties and a transition to the tetragonal phase.

Hot stage X-ray diffraction [3,5] showed that the lattice parameters of YBa$_2$Cu$_3$O$_{7-δ}$ expanded linearly up to 500°C, with a thermal expansion along the c axis that is nearly twice that along the a and b axes. Above 500°C, however, the b axis contracts and the a axis expands at a superlinear rate. Finally the a and b axes become equal and YBa$_2$Cu$_3$O$_{7-δ}$ is tetragonal. The temperatures at which the thermal expansion deviates from linearity and at which the orthorhombic to tetragonal transition occur are very dependent on the oxygen partial pressure [5]. Thermogravimetric studies have shown that O$_7$ starting material begins to lose oxygen reversibly above ~350 – 400°C. The orthorhombic to tetragonal transition is assumed to occur where there is a discontinuity in the curvature of weight loss versus temperature plots.[7]

In situ neutron diffraction [4] showed that the observed temperature dependent changes in lattice parameters are caused by changes in oxygen content and order on the basal copper plane (between the barium layers). The oxygen that is lost above ~400°C comes primarily from the O(1)[= (0, 1/2, 0)] site, resulting in the negative thermal expansion of the b axis before the transition. Part of the oxygen that is removed from the O(1) site goes on the normally vacant (1/2,0,0) site, resulting in the enhanced expansion along the a axis just below the transition. These results show that the oxygen arrangement changes from fully ordered, at room temperature, to partially ordered, at elevated temperatures, in the orthorhombic phase, to completely disordered at still higher temperatures in the tetragonal phase. Oxygen continues to be depleted from the basal copper plane above the transition.

There is no doubt that the orthorhombic-to-tetragonal transition is an order-disorder transformation. However it is not yet clear whether the phase change is a classical Gibbsian first-order phase change or is a second order transformation.

When oxygen is removed from O$_7$ starting material at low temperatures, the loss of superconductivity does not always coincide precisely with the
orthorhombic-to-tetragonal phase transition. In these samples $T_c$ typically drops to zero between $O_{6.5}$ and $O_{6.4}$, but the orthorhombic-to-tetragonal transition may occur at still lower oxygen contents. Several bond lengths change rapidly just before the transition, such as the Cu(1) — O(4) and Cu(2) — O(4) bonds. Consequently it has been suggested that these bonds may play a role in superconductivity. However, because several distances are changing simultaneously, it is not clear at the present time which, if any, is critical for high $T_c$.

The simultaneous loss of metallicity and superconductivity is a property which is quite unique to the oxide superconductors,[59-61] and in particular to the cuprate superconductors. The stoichiometry of oxygen has been considered to be the crucial parameter governing the superconducting transition temperature $T_c$, of the YBa$_2$Cu$_3$O$_{7-x}$ family of superconductors. The transition from the superconducting to the non-superconducting state is accompanied by a metal insulator transition. There is also a crystallographic phase transformation since the crystal structure in the superconducting phase is orthorhombic but changes to tetragonal in the non-superconducting phase.

A large amount of experimental work [62-85] has been concerned with establishing a correlation between the decrease in orthorhombicity and $T_c$ as a function of increasing $\delta$. On the other hand, the theoretical investigation[66-67] of the phase diagram of YBa$_2$Cu$_3$O$_{7-\delta}$ as a function of $\delta$ has shown that the orthorhombic phase in which the chains are ordered is favoured thermodynamically in the superconducting region. Two types of orthorhombic phases have been proposed to exist predominantly in the superconducting region: ortho I consisting of YBa$_2$Cu$_3$O$_7$ and ortho II consisting of YBa$_2$Cu$_3$O$_{6.5}$. The latter is a fully ordered phase in which the chains are completely ordered in an alternate fashion with full, empty, full... sequence. This results in a doubling of the lattice parameter along the a axis and gives rise to a superstructure which has been identified experimentally.[13,68]

From these investigations it is clear that it is really not the orthorhombicity that is of interest for superconductivity; it is rather the formation of fully ordered chains that is more relevant, and this chain formation along the b axis is reflected in an orthorhombic distortion. Clearly, when the chains are completely broken and disordered and the oxygens have a ran-
dom distribution so that the populations along both a and b axes are equal, the overall crystal symmetry is tetragonal. It is in this structure, which has no chains, that the compounds are insulating and not superconducting. The existence of superconductivity depends upon the lengths of the broken chains and their distribution.

A remarkable property of all cuprate superconductors is the presence of two-dimensional CuO$_2$ planes. The ground state of these compounds is insulating and antiferromagnetic. Superconductivity arises when carriers are created in the CuO$_2$ planes, thus rendering them metallic. The ordering of oxygen atoms in the chains plays a crucial role in controlling the carrier concentration in the CuO$_2$ planes which in turn affects $T_c$. At a local level, it is the coordination geometry around the chain site Cu atom that plays the critical role in controlling the charge transfer from the CuO$_2$ planes [69]. Two-fold, three-fold, and non-square-planar four-fold coordinations of the chain-site Cu atom are not favourable for charge transfer from the CuO$_2$ planes, and the four-fold square-planar coordination is essential for a significant hole carrier density and hence superconductivity to occur.

In the YBa$_2$Cu$_3$O$_{7-\delta}$ family of superconductors the planar Cu(2) atom has a square pyramidal coordination. However, the apical O(6) oxygen atom to which a Cu(2) atom is bonded is $\sim$20% further away than the four O(1), O(2) oxygen atoms in its plane. This much longer Cu(2) - O(6) bond length renders the interaction of the planar Cu(2) atom with the apical O(6) oxygen atom much weaker in comparison to that with the oxygens in its plane, so that in reality the planar Cu(2) atom retains a four-fold square-planar coordination. In superconducting YBa$_2$Cu$_3$O$_{7-\delta}$, Cu(1) - O(6) and Cu(1) - O(4) bond lengths are such that the chain Cu(1) atom has a square planar coordination of its own in the bc plane. It is this rather weak Cu(2) - O(6) interaction that confers on these materials a two-dimensional character. This leads to the formation of two separate sets of antibonding band complexes in the vicinity of the Fermi level with a rather negligibly small hybridization between them [70-72]: (1) planar CuO$_2$ bands formed between the planar Cu(2)d$_{x^2-y^2}$ orbital and the planar O(1)p$_x$ and O(2)p$_y$ orbitals and (2) the chain CuO$_3$ bands formed between the chain Cu(1)d$_{x^2-y^2}$ orbital and the apical O(6)p$_z$ orbital and the chain oxygen O(4)p$_y$ orbital in orthorhombic YBa$_2$Cu$_3$O$_7$. The relative positions of these band complexes determine the charge transfer between the CuO$_2$ planes and the CuO$_3$ units.
Y and Ba are essentially ionic, acting as electron donors and retaining only a very small charge at their sites. This small charge arises from a very weak hybridization with the neighbouring oxygen, and is in agreement with the generally accepted chemical description of these elements being ionic in nature in these compounds. In the insulating YBa$_2$Cu$_3$O$_6$ the chain-site Cu(1) and the apical O(6) oxygen atoms are in their insulating Cu$^+$ and O$^{2-}$ ionic states, respectively, so that the planar CuO$_2$ bands are half filled. In fact YBa$_2$Cu$_3$O$_6$ is an antiferromagnetic insulator, and a Mott-Hubbard description is certainly more appropriate. Because of the insulating character of YBa$_2$Cu$_3$O$_6$ the total charge on a CuO$_2$ plane in this compound provides a natural reference for calculating the charge transfers from the CuO$_2$ planes in different crystallographic situations, and this charge transfer corresponds to the hole concentration in the CuO$_2$ planes with respect to the insulating ground state. Stoichiometry in oxygen is not a sufficient condition for determining the hole concentration in the CuO$_2$ planes, the local coordination geometry around the chain-site Cu(1) atom plays a deciding role in controlling its value.

The charge transfer from the CuO$_2$ planes in these compounds depends on a delicate balance between the positions of antibonding band complexes formed by the CuO$_2$ planes and those by the CuO$_3$ units. In YBa$_2$Cu$_3$O$_6$, the chain Cu(1) atom interacts essentially with the $p_z$ orbitals of the apical O(6) atoms through its $d_{xz}$ orbital. The antibonding band which is formed through this interaction falls below the Fermi level. This leaves the antibonding bands formed by the planar CuO interactions exactly half full. In the superconducting YBa$_2$Cu$_3$O$_7$, the addition of O(4) oxygen atoms to form chains along the b axis leads to the formation of two nonbonding O(4)$_{p_x}$ and O(4)$_{p_y}$ levels which lie below the Fermi level. Further, the interaction of the O(4)$_{p_y}$ level with Cu(1)$(d_{xz})^2$ level, which was occupied in YBa$_2$Cu$_3$O$_6$ and now properly designated as Cu(1)$(d_{xz})^2$, gives rise to an occupied bonding Cu(1)$(d_{xy} - p_y)^2$ - O(4)$_{p_y}$ level, and the corresponding antibonding part in the vicinity of the Fermi level. Thus the presence of the chain O(4) oxygen atoms results in the formation of three additional bands. However, an O(4) oxygen atom brings only four $p$ electrons. This leaves the antibonding band in the vicinity of Fermi level nearly empty. If this band was fully empty, falling above the Fermi level, there will again be no charge transfer from the planar CuO$_2$ antibonding band, which will remain
half filled as in YBa$_2$Cu$_3$O$_6$. However, in superconducting YBa$_2$Cu$_3$O$_7$, the bottom of this band falls below the Fermi level. This leads to a lowering of the Fermi level and an electron transfer from the planar CuO$_2$ bands so that the Fermi level can be equalized.

It was proposed that the transition from orthorhombic to tetragonal symmetry and the dramatic depression of $T_c$ were the result of the destruction of the one-dimensional Cu — O chains.

Initial neutron diffraction studies of the tetragonal phase were done on the samples with compositions near YBa$_2$Cu$_3$O$_6$ in which the chain oxygen atoms were completely removed [73-74]. In most cases, these samples were synthesized by cooling in an inert atmosphere. More recent studies show that the oxygen stoichiometry is a continuous function of temperature with the orthorhombic to tetragonal transition occurring near YBa$_2$Cu$_3$O$_{6.5}$[4]. With increasing $\delta$, the one dimensional chains in the orthorhombic phase are disrupted by an increasing number of oxygen vacancies at the O(1) (0,1/2,0) site accompanied by an increasing occupancy at the originally vacant site at (1/2,0,0). At the transition, the occupancy of the originally vacant sites at (0,1/2,0) and (1/2,0,0) is equal to 0.25, giving rise to highly disordered two-dimensional Cu — O network in the basal plane.

The reduction in $T_c$ correlates with the reduction in the oxygen stoichiometry and the associated disordering of the Cu — O chains. In an ionic picture, the oxygen stoichiometry can be related to Cu valence by a simple charge balance argument. Superconductivity disappears near the oxygen stoichiometry corresponding to an average valence of 2+ for the copper ions. In a metallic picture, the oxygen stoichiometry affects the electronic behaviour by shifting the Fermi level and altering the underlying band structure. In a simple rigid-band picture, removal of oxygen increases the number of conduction electrons and raises the Fermi level. (This increase in the Fermi level is equivalent to decrease in the average copper valence in an ionic picture.) If the density of states at the new Fermi level were lowered, the superconducting transition temperature would be expected to fall [75]. In addition to a shift of the Fermi level, oxygen vacancies will cause a change in the band structure itself, since the vacancies remove an important overlap in the one dimensional metallic Cu — O chains. In general, one expects the one-dimensional bands associated with the chains to narrow, leading to a higher density of states. Both, a Fermi level shift and changes
in band structure due to oxygen vacancies, play a role in determining the final density of states. It should be noted that the mechanisms governing superconductivity in the high $T_c$ oxides are not understood so that effects other than variations in the density of states may be important. Nevertheless, it is likely that the reduction in $T_c$ and the structural transition itself are driven by the electronic energy of the system.

It is a remarkable feature of the quenched samples that the geometry of two-dimensional Cu-O planes is relatively unaffected as the quench temperature is varied. It is therefore tempting to conclude that only the chains are involved in the superconductivity. However, there are important electronic interactions between the chains and the planes mediated by a bridging oxygen on the O(4) site. Thus changes in electronic structure caused by the oxygen vacancies in the chains may affect the electronic behaviour of the planes in a way that is detrimental to superconductivity. Therefore, the role of two-dimensional planes in the superconductivity cannot be directly addressed with previous results. In contrast, the role of the chains is clear: superconductivity is weakened as the one-dimensional chains are disrupted, and the transition temperature goes to zero when the $(0,1/2,0)$ and $(1/2,0,0)$ sites become symmetry equivalent and reach an average occupancy of 25%. The presence of chains is essential for achieving a high transition temperature.

It has been generally held from the start that the unusual properties of YBa$_2$Cu$_3$O$_{7-\delta}$ originate from the chemistry of copper; to be precise, from its ability to create numerous metal-oxide-type phases characteristic of oxygen non-stoichiometry—a crucial parameter for the extended domains of existence within the appropriate phase systems.

A direct consequence of the different valency states of copper, changing within the homogeneity range of a given phase, is a dramatic change in the transport properties of the phase. All this happens because of a specific level of oxygen deficiency.

The rich source of experimental data already available in literature [76-77] indicates that, although some substantial differences in crystal structure and physical properties occur, the superconductors exhibit several common features. The most prominent are:

1. Insensitivity of $T_c$ to the chemical nature of the rare earth element substituted for yttrium, thus indicating little interaction between rare-earth...
ions and the conducting electrons;
2. sensitivity of $T_c$ to copper substituents;
3. great sensitivity to oxygen concentration.

The features outlined above indicate that superconductivity in these oxides is realized through either Cu — O planes, which exist in both types of structures and/or through the Cu — O chains present in YBa$_2$Cu$_3$O$_{7-\delta}$ phase, changing with the valency of copper ions according to the phase's overall oxygen content.

Systematic studies of compositional dependency of YBa$_2$Cu$_3$O$_{7-\delta}$ and its physical properties, dominate the literature. At present, the following general opinions on the YBa$_2$Cu$_3$O$_{7-\delta}$ phase are held. The range of homogeneity extends from $\delta = 0$ to $\delta = 1$. The phase is at the most orthorhombically distorted (Pmmm) for an oxygen index close to 7. With increasing $\delta$, distortion decreases. At $\delta = 0.5$, the phase becomes tetragonal (P4/mmm) and keeps this symmetry upto $\delta = 1$. The structure transition at $\delta = 0.5$ is considered to be an order-disorder type and takes place at 700°C, dependent on ambient partial pressure of oxygen in the phase. The general rule is that the higher the external pressure of oxygen, the higher the transition temperature.[4]

At an external pressure of oxygen not exceeding one atmosphere, the phase starts to undergo thermal decomposition (loss of oxygen) at about 540°C. At 900 — 950°C, the phase's oxygen index reaches a minimum of about 6. Below this value a phase separation occurs. Sensitivity of the phase to self oxidation depends mainly on its starting oxygen index, and for an oxygen pressure of one atmosphere it becomes noticeable at about 250°C for samples with $\delta \leq 1$, at about 370°C for those with $\delta = 0.5$ and for others with $7 - \delta \geq 6$ full oxidation can be achieved close to 500°C. Above this temperature, thermal decomposition begins in exactly the reverse manner.[76-77]

### III.5 Results and Discussion

The purpose of this work was to determine the lattice parameter and homogeneity range of YBa$_2$Cu$_3$O$_{7-\delta}$ with the phase's oxygen content, and to express its influence on $T_c$. 

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Fig III.5
Fig. III.6  Plot of Transition temperature (Tc) vs Oxygen content (γ-d)
Fig. III.7  R-T plots for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples
Y 123 C

Temperature (K)

Resistance (m-Ohms)
Fig III.8 Variation of lattice constants with oxygen content
The specimens were characterized by X-ray powder diffraction analysis. X-ray diffraction patterns of the YBa$_2$Cu$_3$O$_{7-\delta}$ samples are shown in Fig.III.5. The oxygen concentration is related to the c dimension as

$$7 - \delta = 67.108 - 5.161 \times c(A^\circ)[7]$$

The lattice parameters, oxygen content and T$_{c}$s of the samples are presented in table III.1. Fig.III.6 shows the resistive transition temperature Vs oxygen concentration plots of YBa$_2$Cu$_3$O$_{7-\delta}$. Although fairly sharp transitions have been observed in our specimens, the superconducting transition displays systematic variation. Resistivity plots (Fig.III.7) show that as the oxygen is removed from the pure sample, the onset of superconductivity lowers and becomes progressively broader. For the value of $7 - \delta = 6.26$, superconductivity is virtually destroyed. Hence we can conclude that a large deficiency of oxygen destroys the superconductivity.

A distinct change in the nature of resistivity is also apparent with the change in oxygen stoichiometry, transforming from metallic ($d\rho/dT > 0$) in the case of the first three samples to semiconductor - like ($d\rho/dT < 0$) for the fourth sample. The superconducting to semiconducting behaviour is reversible and varies directly with oxygen stoichiometry.

Fig.III.8 shows the variation of lattice constants a, b and c with oxygen concentration. Little change is observed when the reducing temperature is less than about 400°C. For a temperature of 450°C a transformation from orthorhombic to tetragonal occurs. With a decrease in oxygen content, a axis expands while b axis contracts and c axis expands monotonically. However, a complete conversion to the tetragonal phase is not observed and the data is not quite systematic.

As $T_c$ depends on oxygen stoichiometry, changes which occur with reduction may provide the key to the superconductivity in these materials. The most dramatic effect of oxygen removal is loss of connectivity in the 1D chains that run along the b axis. This may indicate that conductivity occurs along these chains. An alternate explanation involves valence fluctuations of the copper atoms [8]. Such fluctuations depend on the displacement of O(1) between Cu(1) and Cu(2). This model has many common features with the bipolaron ideas that originally motivated the search for superconductivity in the ternary copper oxides by Bednorz and Müller. The
movement of O(1) towards Cu(1) upon reduction will make these fluctuations less likely. Regardless of the exact mechanism, it is clear that the 1D chains play a vital role in superconductivity, either by modulating the 2D layers or by carrying the superconducting current.

In contrast to the references cited earlier, there is no evidence for a sharp collapse in the symmetry of the phase at $7 - \delta = 6.5$. There seems to be a linear and continuous decrease of the orthorhombic distortion, in this respect, our results resemble much those reported by Cava et al [62] and Bukowski et al [78] where quite different preparation techniques were applied.

Concerning the superconducting behaviour of YBa$_2$Cu$_3$O$_{7-\delta}$, we can state that it is not entirely connected with the orthorhombic structure. As can be seen, superconductivity disappears before the oxygen content at which transition to the tetragonal structure occurs is reached. This means that superconductivity is limited to a minimum value of the orthorhombicity. It looks as if there is little correlation between $T_c$ and the oxygen index and it seems that there must be another factor (or factors) interfering with such a possible correlation.

It is known that by heating in a reducing atmosphere, low oxygen indices are obtainable. Those of higher values require a lower temperature. Consequently, the probability for temperature-induced statistical distribution of oxygen atoms, within the Cu-O chains of the central structure plane, will decrease as the oxygen index decreases. It is obvious that such disordering will result in a diminishing of the orthorhombic distortion, characteristic for the YBa$_2$Cu$_3$O$_{7-\delta}$ phase of a given oxygen content. This makes the distortion dependent on two parameters: the oxygen index and the oxygen atom disordering. In this way it becomes highly probable that the simultaneous influence of these parameters may result in a more or less rapid collapse of the symmetry.

If carefully prepared, the phase should exhibit the orthorhombic symmetry throughout the range of its existence. The level of distortion should change linearly with the oxygen index, from a maximum value at 7.0 to zero at 6.0. Any deviation from this rule will reflect the effect of temperature induced oxygen atom disordering, quenched within the structure by the specific preparation procedure applied. Our results seem to reflect just an intermediate state, i.e. a contribution from oxygen disordering to the
Fig. III.9 Lattice parameters and oxygen index of Y123 - a comparison with experimental data available in literature.
naturally decreasing orthorhombic distortion of the phase, caused by the decrease in its oxygen index.

In order to prove this further, we present a comparison of the phase lattice parameters of our samples and those obtained from different sources[62,75], plotted versus the oxygen index (Fig III.9). The appropriate data are arbitrarily gathered inside an angle, the arms of which reflect an ideal behaviour. This ideal behaviour might be expected if the orthorhombic distortion exhibits a linear dependence on the oxygen index (if the phase is not sensitive to oxygen atom disordering). Therefore an increase in contribution of the disordering with decreasing oxygen index is noticeable.

As expected, beginning from an oxygen index close to 6.5, disordering can become dominant. This is quite reasonable since thermal hopping of less than half an oxygen atom per unit cell should be much easier than at the higher ratios. Easy thermal excitation of the oxygen atoms in the Cu—O ribbons [79], together with the quenching technique of preparation, must lead to a situation in which, starting from certain oxygen indices, one can obtain a series of samples characterized by different levels of orthorhombic distortion, including the tetragonal form.

Fig III.9 represents sufficiently large numbers of experimental data to allow another important feature of YBa2Cu3O7-δ to be seen. It is easy to notice that, beginning from an oxygen index close to 6.75, the linear increases and decreases of the a and b parameters respectively are evidently stopped. Since the increase reflects the incorporation of additional oxygen atoms to, still partly filled, Cu—O chains existing along the b axis, we conclude that inspite of the increase in overall oxygen index, the upper limit of fractional occupancy of the (0,1/2,0) atomic sites is 0.75, the remaining portion of oxygen atoms (0.25) being located in (1/2,0,0) sites.

Assuming that for higher concentration of oxygen in the phase, the contribution of the b-axis Cu—O chains to the mechanisms of superconductivity is bigger than the contribution resulting from the Cu—O planes existing between the yttrium, and barium ion layers, another valuable conclusion arises as a consequence. This is that the oxygen index interval 6.75-7.0 must be characteristic of constant Tc values which, in addition, should correspond to the upper limit of Tc found so far for YBa2Cu3O7-δ.

In order to study the effect of oxygen atom disordering on Tc we decided
to express the appropriate values in terms of the orthorhombic distortion parameter $p = (b - a)/(b + a)$. It has been shown that superconductivity in the YBa$_2$Cu$_3$O$_{7-\delta}$ phase disappears entirely if either the orthorhombic distortion parameter, $p$, is less than $3 \times 10^{-3}$ or the oxygen index is less than 6.3. As can be seen in the case of our fourth sample (Y123C) even though $p > 3 \times 10^{-3}$, ($p = 4.4 \times 10^{-3}$), superconductivity disappeared since oxygen index is less than 6.3. We conclude that in this case the loss of superconductivity is a result of a large level of oxygen deficiency in the sample of orthorhombic symmetry.

It has generally been reported that YBa$_2$Cu$_3$O$_{7-\delta}$ changes from orthorhombic to tetragonal symmetry for an oxygen index less than 6.6. However, those data have either been obtained at elevated temperatures, or for samples quenched from higher temperatures than those employed here. The extension of the orthorhombic symmetry beyond $7 - \delta = 6.3$ depends upon the thermal conditions employed to obtain the oxygen stoichiometry. Samples prepared at higher temperatures are not likely to display the features discussed here. We conclude that the spatial arrangement of the oxygen atoms, and not only their average concentration, determines the superconducting transition temperature.
<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Tσ</th>
<th>7 − δ</th>
<th>p</th>
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<tbody>
<tr>
<td>Y123</td>
<td>3.818</td>
<td>3.890</td>
<td>11.660</td>
<td>91.0</td>
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<td>3.876</td>
<td>11.670</td>
<td>66.0</td>
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<tr>
<td>Y123A</td>
<td>3.839</td>
<td>3.730</td>
<td>11.790</td>
<td>−</td>
<td>6.260</td>
<td>4.4 × 10⁻³</td>
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References


